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### FD163: Photo-initiated Molecular Quantum Dynamics

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## DISCUSSIONS

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## General discussion

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**Professor Whitaker** opened the discussion of the paper by Professor Herek by communicating: I would just like to make a quick observation and then I have a more substantive question. What you call “Passive Control” seems to me to be just a fancy way of saying “Chemistry”. I’m a little unclear if your aim to use coherent control to inform chemistry or chemistry to inform control strategies? Perhaps both?

My real question concerns Fig. 8, particularly the bottom right panel. As you write in the paper the shape of the response as a function of the wavelength of the phase-flip is remarkably reminiscent of Meshulach and Silberberg’s classic *Phys. Rev. A* paper (your ref. 11) in which they examined a two photon response in atomic Cs vapour. You take this as supporting evidence for a multiphoton control mechanism. But the constructive interference observed by them for a 180 degree phase-flip in the centre of the excitation spectrum is the consequence of non-resonant two-photon (more generally N-photon) excitation, and this seems to contradict your chirp data, which would suggest to me a wavepacket following mechanism *via* a detuned resonance. Can you rationalise these two seemingly opposing views?

**Professor Herek** communicated in reply: Professor Whitaker’s remark is correct; in this case, passive control refers to chemical modifications on the periphery of the molecule that affect the binding interaction and thereby the chemical reactivity. In particular, these modifications may result in substantial changes in the forward and backward electron injection rates thereby providing an effective mechanism of passively tuning the functional efficiency.

In general, passive control refers to all of the modifications that are made to the system or environment (*i.e.* temperature, pH, synthetic design of reactants, *etc.*) at the onset in an attempt to modify the outcome of the reaction, whereas active control implies engaging with the system during the reaction itself so as to influence directly the evolving dynamics. Coherent control is a subset of active control in which quantum coherence effects play a role. These are generated by tuning laser pulse parameters such as the phase, amplitude and polarization of individual frequency components to manipulate the generation and evolution of the excited state wavepacket.

Overall, our aim is to use both active and passive control strategies to gain fundamental insight into excited state dynamics of molecules, and the underlying factors that govern these.

Regarding the “w” shape observed in the  $\pi$ -phase-step scan, we were indeed inspired by the classic work of Meshulach and Silberberg<sup>1</sup> in suggesting that this behavior reflects a two-photon (or potentially N-photon) control mechanism. Likewise, the chirp scan results also imply a two-photon pump-dump control mechanism, analogous to that explored in early experiments by Bardeen and Wilson.<sup>2</sup> The former is generally a non-resonant interaction, while the pump-dump process tracks a wavepacket on an excited state potential energy surface. Note that for both the  $\pi$ -step and chirp scans (see Fig. 8), the control yield was much smaller than was found in the blind optimization. For such a complex system of a large organic molecule in the condensed phase, it is likely that many different control mechanisms are at play. The systematic open-loop scans presented here suggest two of them.

1. D. Meshulach and Y. Silberberg, *Nature*, 1998, **396**, 239.

2. A. H. Buist *et al.*, *Opt. Lett.*, 1999, **24**, 244.

**Professor Fielding** communicated: Professor Herek has presented a beautiful illustration of both active and passive control. Would she be able to comment on the possibilities for exploring links between the two methods, *i.e.* learning from active control experiments how and what passive control methods might be realised to achieve a particular goal?

**Professor Herek** communicated in reply: I appreciate this comment and the excellent question, if not proposition, to further explore the powerful combination of active and passive control strategies as a means for obtaining deeper understanding of photophysical processes and chemical reaction mechanisms. Insights gleaned from active control experiments, in particular open-loop studies in which specific pulse shapes (*i.e.* chirps, pulse trains,  $\pi$ -steps) are scanned, can reflect features of the potential energy landscape or identify key vibrational modes. These are precisely the sorts of parameters than can be fine-tuned by passive control strategies involving chemical modification.

**Professor Field** communicated: Spin-orbit is one of my favorite topics. Owing to its exceptionally atom-localized character, spin-orbit is useful in formulating an atom-in-molecule picture of electronic structure or in devising numerically specific modifications of dynamical processes. For example, by replacing the Zn atom in your ZnPc molecule, you could scale the spin-orbit interaction strength up or down by a known amount (see Table 5.6 on pages 316–317 of “The Spectra and Dynamics of Diatomic Molecules,” H. Lefebvre-Brion and R. W. Field, Elsevier, 2004). This would allow you to modify the rate and mechanism of Inter-System Crossing. My question concerns how ISC is exploited in your active control schemes. If the spin-orbit constant is small, then the existence of spin-mixed states will depend on accidental degeneracies between vibronic levels of singlet and triplet states. Most eigenstates will be nearly pure singlet or nearly pure triplet, and population transfer between singlet and triplet will occur only *via* the small number of spin-mixed levels. It seems to me that this is a good situation for cleverly designed control schemes. If the spin-orbit constant is large, then nearly all vibronic states will be of spin-mixed character. In such a case, population will flow between nominal singlet and triplet levels promiscuously. There will be little

opportunity for control schemes to modify the rate or efficiency of singlet to triplet population transfer. It would be very interesting if you could compare active control schemes for ZnPc to those for CdPc and CaPc.

**Professor Herek** communicated in reply: This is an excellent suggestion for a passive control scheme that exploits spin-orbit coupling to modify reaction dynamics, and presents a nice case for combining active and passive control strategies. At this point in our studies, we don't really know how ISC is exploited in the active control scheme, if at all! After all, ISC occurs on a very slow time scale in ZnPc; our feedback window for this path is some 20 ns after the excitation pulse. Comparing the control yield in ZnPc with its Cd- and Ca- siblings, could be very insightful. It would also be interesting to study systems which exhibit ultrafast spin dynamics, on a comparable timescale as the vibrational dynamics.

**Professor Buma** communicated: In your experiments you observe after optimization a certain ratio for the T/S ratio of ZnPc. Can you say *a priori* anything about what values should theoretically be possible and what the limits would be? Or, put in a different way, how does one know that the ratio that you have obtained is the best one possible? Would it be, for example, possible that if you would have started with a completely different set of phase and intensity values that you would have ended ten times as high?

**Professor Herek** communicated in reply: It's unlikely that the result of a blind optimization experiment is "the best one possible", and even more so that starting with a different set of random phase and intensity values would yield an order of magnitude difference in the control yield. Most likely, the real optimum lies somewhere in between. Not only do learning algorithms need to be sufficiently smart in efficiently sampling the enormous multidimensional parameter space, but limitations of the spatial light modulator preclude many solutions. Furthermore, as discussed before, there may be many possible control mechanisms. Hence any result can be a good result, if we can discern how the corresponding pulse shape acts on the system to induce a change in the reaction outcome.

**Mr Arruda** communicated: In Fig. 5, you show some X-FROG traces of optimized pulses with strong features that span several hundred femtoseconds, and up to a picosecond in Fig. 5d. How do you determine your time resolution and effective *t*-zero position? Does it even matter to you in the context of these measurements?

**Professor Herek** communicated in reply: The X-FROG traces are made by cross-correlation of the shaped pump pulse and a well-characterized transform limited unshaped reference pulse containing the same power spectrum and with duration of 25 fs. The reference pulse traverses the same path length as the supercontinuum probe pulse, and is overlapped with the pump in a nonlinear crystal placed at the sample position, hence the effective time zero is sufficiently well defined (especially in the context of the measurements, where the control effect is probed at times of 25 ps and 20 ns after the shaped excitation pulse).

The temporal resolution is determined by the FWHM of the cross-correlation signal at time zero.

**Professor Riedle** communicated: How far into saturation is your experiment performed? The reason this seems most important to me is the following: if you go close to saturation, any extra pump energy will not increase the excitation level. This is at least true if your pulses are longer than the electronic dephasing time. However, if the excited state vibronic wavepacket moves away from the Franck–Condon point sufficiently to loose resonance with the pump pulse, you basically start your excitation process again from a pure ground state - yet diminished - sample and can propagate further population into the excited electronic state. Could such a scenario explain your measurements? Is the spacing between sub-pulses appropriate and/or the chirp counterproductive for one sign and productive for the other? Such a chirp dependence has been utilized in early experiments of Bardeen and Wilson.

**Professor Herek** communicated in reply: The experiments are performed with an excitation intensity corresponding to the onset of saturation, where the scenario described by Prof. Riedle is indeed occurring in our sample. The strongest evidence for this lies in the initial 6% jump in the T/S ratio seen in Generation 1 of our blind optimization experiments (Fig. 5). This step-wise increase of the fitness value at the onset of the learning curve occurs concomitant with a 50% loss in actinic energy, and reflects a spreading of the pump intensity to allow for multiple excitation processes. However, beyond this initial (trivial) control mechanism, the fitness continues to climb even though the actinic energy does not vary. This further tweaking of pulse shape implies the involvement of more complicated mechanisms than just signal saturation.

**Professor Reid** communicated: If it were possible to achieve substantial active control of the photodynamics in zinc phthalocyanine, would it be possible for this to be used in practice in photodynamic therapy?

**Professor Herek** communicated in reply: I guess this would depend on how substantial the control, and how simple the optimal pulse shape. At the moment, our aim is to extract insight on the mechanisms of photodynamic therapy, to identify the factors that determine efficiency and eventually enhance these by, *e.g.* chemical modification. We're not looking to bring shaped pulses into the clinic. But perhaps that day is not so far off. Mosk and co-workers are developing other shaping strategies—sculpting the wavefront of propagating light—to overcome the problems of scattering in turbid media, that may revolutionize medical optics. Adding spectral shaping will open even more possibilities.

To note, ZnPc is already being used in clinic trials of photodynamic therapy, as it has a high absorption cross-section in the red/near-infrared region where human tissue is most penetrable. The efficiency, however, is limited by an ISC yield of only 60%.

**Professor Meier** communicated: Do you expect the ISC to be favoured when exciting to higher lying states?

**Professor Herek** communicated in reply: I expect that by engaging higher excited states, we have access to more pathways, including some that will ultimately lead to ISC. Hence I think that by accessing these states *via* multiphoton excitation, we can enhance the ISC yield.

**Professor Riedle** communicated: In the experiments reported by Prof. Herek, the aim is to improve the singlet oxygen yield. As desirable as this might be, I'm wondering whether this type of control experiment is not going in a direction that does not make best use of the technical capabilities. One tries to optimize a quantity that is already produced in a fairly large amount by a Fourier-transform-limited pulse. As the shaper diminishes the pulse energy considerably, it would be much easier to increase the total yield of the experiment by just using the unshaped pulse.

A different case would be given if the photochemical reaction under investigation has two more or less equally likely outcomes. If one of them is highly undesirable, coherent control should try to minimize it. In this way a much larger effect could be reached. To find proper examples, one can simply consult the large body of photochemical literature and look at those examples that have a good total quantum yield, but not the selective outcome desired. Experienced photochemists will readily be able to point out such "misbehaving" systems.

**Dr Blancafort** communicated in reply: Our contribution on the control of fulvene photophysics goes in the direction pointed out by Prof. Riedle. It is a molecule where the decay to the ground state can take place with or without rotation of the double bond. Under normal conditions, the decay without rotation is favored, and our goal is to simulate conditions where we force the rotation of the double bond to be the favored process.

Moreover, what makes fulvene an interesting model system is that the competition between two photochemical processes takes place along a seam of intersection, and we try to use this mechanistic knowledge to derive a control scheme. This seems to be quite a general situation. For example, we find that the competition between the stepwise and concerted paths in the light-induced Wolff rearrangement also takes place along a seam [Q. Li, A. Migani, L. Blancafort, *J. Phys. Chem. Lett.*, 2012, 3, 1056–1061]. Therefore, understanding the dynamics at the seam is essential to derive viable control schemes for photochemical reactions.

**Professor Stolow** communicated: Space-time coupling at the focus of an electromagnetic field is an unavoidable consequence of using a spatial light modulator, such as in a typical '4f' arrangement. How does one ensure that such effects do not alter the interpretation of a given control mechanism?

**Professor Herek** communicated in reply: I appreciate this question, which highlights a serious consideration for this sort of experiment. I think Prof. Stolow answered it best himself in his recent publication on the topic.<sup>1</sup> We recognize that the applied field of the shaped pulses can vary spatially in the focal plane. Even in the absence of pulse shaping, a misaligned NOPA can create significant spatial chirp. As such, different target molecules can experience different excitation fields, thereby smearing the control effect, and the observed control effect can depend on the overlap of the probe laser. For this reason, we focus the probe laser to a much smaller diameter than the pump, and optimal pulse shapes are tested for robustness by repeated scans, sometimes days/weeks after the original optimization was performed. Further, we monitor how the fitness level varies when tweaking the pump–probe overlap, to confirm that no significant spatial variations. The space-time coupling can be experimentally determined from the spatial

intensity distribution (e.g., with a CCD camera) and the spectrally resolved intensity distribution (by scanning the entrance slit of a spectrometer across the image of the focal plane).

1. B. J. Sussman, R. Lausten and A. Stolow, *Phys. Rev. A.*, 2008, 77, 043416.

**Professor Temps** opened the discussion of the paper by Professor Bañares by communicating: Repulsive potential energy surfaces may be hard to investigate by direct measurements starting in the electronic ground state. Could your experiments provide a general methodology to characterize elusive repulsive potential energy surfaces? In particular, you could also change polarizations to observe anisotropies, which would tell you about the symmetries of unknown repulsive states.

**Professor Bañares** communicated in reply: In principle, we are limited to study one-photon optically allowed transitions as those typical in methyl iodide to the A-band ( $^3Q_0$ ,  $^1Q_1$  and  $^3Q_0$  repulsive states) which have enough oscillator strength. Of course, we may access other one-photon dark electronic surfaces by, for instance, two-photon absorption if that is optically allowed, and I am thinking in the  $3p_z$  or  $4p_z$  Rydberg states of the methyl radical. Changing polarization using velocity map imaging would not help because doing so you lose the cylindrical symmetry in the experiment, necessary to perform Abel inversion.

**Professor Fielding** commented: I am interested to hear about the H-atom transfer Professor Bañares observes and wonder if he would be able to provide some information about the timescale of the process.

**Professor Dr Bañares** responded: In the experiments we have carried out a study of the excited state hydrogen transfer in pyrrol–ammonia clusters, we have employed pump–probe laser pulses in the nanosecond timescale. We have not obtained information about the timescales of the H-atom transfer process within the clusters.

**Professor Neumark** communicated: How are you able to calibrate the Stark shift, when the total shift of 13 meV in Fig. 4 is considerably less than your laser linewidth (around 40 meV)?

**Professor Bañares** communicated in reply: In the intensity range of the control laser where the Stark shift calibration is shown in Figure 4 of the paper, the signal from the rings in the images does not disappear completely but it reduces with respect to the situation when there is no control laser. Then, the pump laser is slightly retuned to the blue to recover the full signal and this is the way we obtain the Stark shift as a function on the control laser intensity. Of course, at higher intensities of the control laser for which the Stark shift is larger, the signal from the rings totally disappear, as depicted in Fig. 2 of the paper.

**Professor Domcke** enquired: You observed and discussed the excitation of one quantum of the symmetric stretching mode of the methyl radical. However, the methyl group in methyl iodide is pyramidal, while it is planar in the free methyl radical. Why didn't you observe a strong excitation of the umbrella mode of the methyl radical?



**Professor Bañares** responded: We are selectively detecting the vibrational ground state ( $v=0$ ) of the  $\text{CH}_3$  radical by tuning our probe laser to 333.5 nm, by 2+1 REMPI on the Q branch of the  $0^0_0$  transition through the  $3p_z$  Rydberg state (resonant by two photons). Interestingly, given that we are using a broadband femtosecond laser pulse as probe, we are capable of ionizing the  $\text{CH}_3$  radical produced with one quantum of excitation in the symmetric stretch ( $v_1=1$ ), whose Q branch of the  $1^1_1$  transition is quite close in wavelength and within the bandwidth of the probe laser pulse. Actually, at variance with photodissociation of  $\text{CH}_3\text{I}$  in the A-band, where vibrational activity into the symmetric stretch of  $\text{CH}_3$  is small, in the B-band predissociation, the vibrational activity in this mode is important. We can detect  $\text{CH}_3$  radicals with one or two quanta of excitation into the umbrella mode ( $v_2=1$  and  $v_2=2$ ) just by tuning our probe laser to the blue. The Q branches of the  $2^1_1$  and  $2^2_2$  transitions are at 329.6 nm and 325.7 nm, respectively. We have studied the vibrational activity in both the stretching and umbrella modes when exciting  $\text{CH}_3\text{I}$  to the  $0^0_0$ ,  $2^1_0$  and  $3^1_0$  vibronic bands of the  $^3\text{R}_1$  Rydberg state of the B-band in separate publications and deduce vibrational populations.<sup>1,2</sup> There is indeed substantial vibrational activity in the  $\text{CH}_3$  umbrella mode. However, the present experiment is focussed in the strong field control of predissociation from the  $0^0_0$  band of the  $^3\text{R}_1$  Rydberg state of the B-band yielding  $\text{CH}_3$  in  $v=0$  and  $v_1=1$ . We have performed similar experiments when detecting  $\text{CH}_3$  in  $v_2=1$  and  $v_2=2$ , and qualitatively similar results have been obtained regarding Stark shift, dump and multiphoton dissociative ionization processes.

1. G. Gitzinger, M. E. Corrales, V. Lorient, G. A. Amaral, R. de Nalda, L. Bañares, *J. Chem. Phys.*, 2010, **132**, 234313.
2. G. Gitzinger, M. E. Corrales, V. Lorient, R. de Nalda, L. Bañares, *J. Chem. Phys.*, 2012, **135**, 074303.

**Professor Weitzel** communicated: The methyl radical is known to have a planar equilibrium geometry. The formation of methyl radicals by photodissociation from methyl iodide implies that it should be formed in an excited quantum state of the umbrella mode. The population in the  $v=1$  state of this umbrella mode can easily be probed by REMPI at about 330 nm (see *e.g.* Luther, Troe and Weitzel, *J. Phys. Chem.*, 1990, **94**, 6316–6320). This wavelength appears to be just barely outside the band width of your current fs-REMPI. Have you made any attempts to observe the population of excited umbrella states by shifting the central wavelength of your laser field?

**Professor Bañares** communicated in reply: As mentioned in my previous answer, we have centered our probe laser at 333.5 nm to resonantly multiphoton ionize methyl fragments in the ground vibrational state and, given the bandwidth of the probe laser pulse, also with one quantum of excitation into the symmetric stretch mode. Of course, we can tune our probe laser down to 329.6 nm to probe methyl fragments with one quantum of excitation in the umbrella mode. In our previous works,<sup>1,2</sup> we were able of measuring vibrational populations of the methyl fragment into the different vibrational modes. Regarding the strong field control experiments, we have performed similar experiments when detecting methyl with one or two quanta of excitation in the umbrella mode, and qualitatively similar results have been obtained.



1. G. Gitzinger, M. E. Corrales, V. Lorient, G. A. Amaral, R. de Nalda, L. Bañares, *J. Chem. Phys.*, 2010, **132**, 234313.
2. G. Gitzinger, M. E. Corrales, V. Lorient, R. de Nalda, L. Bañares, *J. Chem. Phys.*, 2012, **135**, 074303.

**Professor Riedle** asked: The bond cleavage of a methylhalide transforms the central carbon from a  $sp^3$  hybridization to a  $sp^2$  one. This means that the fragment has to planarize, a motion that takes some time and possibly leads to vibrational ringing. This has recently been analyzed and demonstrated for the related diphenylmethylchloride.<sup>1</sup> In this system a rather universal 300 fs time constant is found at which the fragment transient signal increases largely due to a change in transition strength with the planarization. How can you tell that in your measurements the sub-ps times are not largely influenced by such a nuclear motion? Is the eigenstate picture really justified or shouldn't one rather think in terms of vibronic wavepackets? Wouldn't this behavior also influence the interaction with the control pulse?

1. B. P. Fingerhut, C. F. Sailer, J. Ammer, E. Riedle and R. de Vivie-Riedle, *J. Phys. Chem. A*, 2012, **116**, 11064.

**Professor Bañares** replied: It is of course correct that the methyl group undergoes planarization in the course of iodine elimination in the dissociation of methyl iodide. Two situations must be discriminated, though: in the rapid dissociation that follows after the transition to the first absorption band (A-band) of methyl iodide, centered around 260 nm, a vibrational wavepacket is formed, mainly in the umbrella mode associated to this geometrical change. Resonant detection of methyl occurs after approximately 100 fs.<sup>1,2</sup> In the case studied here, however, excitation of the molecule occurs to the second absorption band (B-band) around 200 nm, where bound Rydberg states exist. Discrete lines constitute this section of the absorption spectrum, which are the result of vibronic transitions to specific vibrational levels of the excited electronic state.<sup>3</sup> Although they are lifetime broadened, due to the interaction with dissociative surfaces, these transitions are spectrally separated further than the laser bandwidth. Therefore, a molecular vibronic wavepacket cannot be created upon absorption under these conditions, and an eigenstate picture, although not perfect, is most useful. It has been described in the literature that the lifetime of such excited states is strongly dependent on the vibrational level of the Rydberg state,<sup>3,4</sup> with values ranging from 800 fs to 4 ps (significantly longer than the planarization times found in the paper you cited). Interaction with the dissociative continuum and subsequent dissociation does of course create a vibrational wavepacket, which correlates with an important degree of vibrational excitation in methyl, both in the umbrella and the symmetric stretch modes.<sup>4</sup>

1. R. de Nalda, J.G. Izquierdo, J. Durá, L. Bañares, *J. Chem. Phys.*, 2007, **126**, 021101.
2. R. de Nalda, J. Durá, A. García-Vela, J.G. Izquierdo, J. González-Vázquez, L. Bañares, *J. Chem. Phys.*, 2008, **128**, 244309.
3. A. P. Baronavski, J. C. Owrutsky, *J. Chem. Phys.*, 1998, **108**, 3445.
4. G. Gitzinger, M. E. Corrales, V. Lorient, R. de Nalda, L. Bañares, *J. Chem. Phys.*, 2012, **136**, 074303.

**Professor Duxbury** commented: Recently Thire *et al.*, *PCCP*, 2011, **13**, 18485 measured time resolved predissociation of the vibrationless level of the B state of

CH<sub>3</sub>I. In their model one of the routes for predissociation is by spin-orbit interaction with the continuum of the anti-bonding lowest unoccupied molecular orbital localised on the C–I band.

In your study of strong field control of predissociation dynamics of CH<sub>3</sub>I, what role do you envisage for spin-orbit interaction given that the atomic spin-orbit coupling of Iodine is very large?

**Professor Bañares** responded: Spin-orbit coupling is crucial for this system due to the heavy iodine atom both in the A and B bands. Without considering the spin-orbit interaction no crossing between the bound Rydberg state and the valence repulsive state would be produced and no predissociation would take place. No special effect on the predissociation dynamics is expected due to the existence of the strong spin-orbit interaction when the control laser field is present for this molecule.

**Professor Meier** communicated: How does the observed change in the lifetime compare with theory?

**Professor Bañares** communicated in reply: There is no theory available to reproduce the present experimental results thus far. A theoretical simulation of this experiment would be very demanding. High level multidimensional *ab initio* calculations of electronically excited states would be required before any dynamics is calculated, and this is a difficult system to be studied at such high level, considering the heavy iodine atom and the strong spin-orbit coupling present in the molecule

**Professor Ashfold** communicated: Corrales *et al.*<sup>1</sup> offer persuasive evidence that the increased rate of decay from the <sup>3</sup>R<sub>1</sub> Rydberg state of CH<sub>3</sub>I observed when the intense 800 nm ‘control’ pulse overlaps (in time) with their 200 nm pump pulse is due to control-laser-induced depopulation routes (*viz.* a resonant one photon dump transition from the <sup>3</sup>R<sub>1</sub> state to the dissociative <sup>3</sup>Q<sub>1</sub> valence state that correlates to the ground state dissociation limit, and multiphoton dissociative ionisation pathways) rather than a consequence of a dynamic Stark shift. The authors suggest that a simple rate equation model can account for the measured >2-fold decrease in excited state lifetime at the highest control laser intensities. To what extent can this same approach account for the deduced variation in the quantum yield of CH<sub>3</sub> + I\* products over the same range of control laser intensities?

1. M. E. Corrales, *et al.*, *Faraday Discuss.*, 2013, **163**, DOI:10.1039/C2FD20143G .

**Professor Bañares** communicated in reply: The quantum yield of CH<sub>3</sub>+I\* products ( $\phi^*$ ) is significantly affected by the opening of the one-photon dump transition from the <sup>3</sup>R<sub>1</sub> state to the dissociative <sup>3</sup>Q<sub>1</sub> valence state. This dissociative state correlates with CH<sub>3</sub>+I products and, thus, the dump process, which is control laser intensity dependent, provides a way to decrease  $\phi^*$  significantly. The answer to your question is yes, the same rate equation model can account for the variation (decrease) of the  $\phi^*$  quantum yield as a function of the control laser intensity.

**Professor Meier** asked: The best control seems to be achieved with a pump/control delay which is not zero. Is this delay experimentally significant? If yes, is there a specific reason for this delay?

**Professor Bañares** replied: The control laser pulse has 4 picosecond duration whereas the pump laser is about 300 fs duration. This means that there is no clear way to define time zero between such pulses. In our experiments, the zero delay time between the pump and the control laser pulses has been chosen at an arbitrary position of overlap between the fs pump and ps probe pulses. For the experiments controlling the lifetime, a pump-control delay time of -1 ps (in our arbitrary scale) has been chosen to ensure that predissociation occurs during the flattest part of the control pulse, since the intrinsic predissociation lifetime is 1.5 ps and the control laser pulse is 4 ps in duration.

**Professor Buma** communicated: In your paper you show that your idea to control the photodissociation of  $\text{CH}_3\text{I}$  at the origin of the B absorption band is compromised by a pump-dump channel that yields  $\text{I}^2\text{P}_{3/2}$ . In this respect control *via* higher-lying excited states such as the C state or even higher lying states might be energetically more favourable. One-photon excitation of these states would not be possible, but previous REMPI-PES studies<sup>1</sup> have shown that they can be excited without any problem using two-, three- or even four-photon excitation.

1. M. R. Dobber, W. J. Buma, C. A. de Lange, *J. Chem. Phys.*, 1993, **99**, 836.

**Professor Bañares** communicated in reply: You are right that it would be interesting to try this control strategy in the C state. However, to reach the C state you need a 180 nm photon, which is far beyond our experimental capabilities. A two-photon absorption using a 360 nm pump pulse would be worth to try. However, you would really need high intensity and thus, using femtosecond pulses, more than two photons could be absorbed and ionize the molecule, having dissociative ionization. I see this as a difficult experiment since you cannot control easily the number of photons absorbed by the molecule when using femtosecond pulses.

**Professor Neumark** opened the discussion of the paper by Professor Weitzel by communicating: In describing the isotope effects in your paper, you conclude that "control between  $\text{H}_3^+$  and  $\text{H}^+$  ... is operative prior to the hydrogen scrambling." Can you explain in more detail what is going on here in terms of isomerization and dissociation barriers?

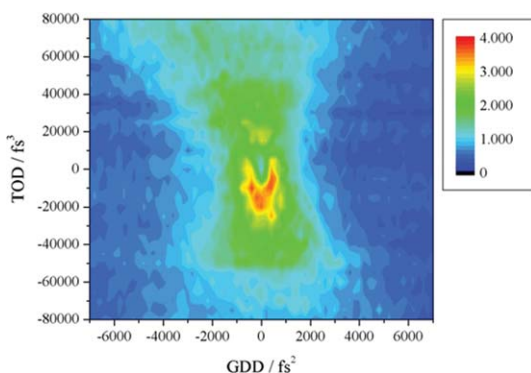
**Professor Weitzel** communicated in reply: All the evidence we have suggests that there is a barrier for hydrogen scrambling in the ethane dication lying energetically below the transition state for breaking into  $\text{H}_3^+$  and  $\text{C}_2\text{H}_3^+$ . This barrier for scrambling connects the isomeric structures  $\text{CH}_3\text{DCD}_2^{++}$ ,  $\text{CH}_2\text{D}_2\text{CDH}^{++}$  and so on.

**Professor Field** enquired: In your paper you mentioned different effectiveness of upward *vs.* downward linear chirps. Have you attempted downward followed by upward "V" chirps or upward followed by downward "lambda" chirps?

**Professor Weitzel** responded: This is an interesting question. Chirping femtosecond laser pulses is a systematic way of shaping the pulse form.

In the current work we have considered the role of linear chirp. We have also investigated the role of quadratic chirp (third order dispersion), but basically all ion yields exhibit maxima for quadratic chirp parameters  $\beta$  close to zero (work to be published). Interestingly for certain objectives, *e.g.* maximizing the  $\text{H}_3^+$  ion yield, optimizing the laser field by means of a genetic algorithm leads to a pulse shape consistent with the dominance of a linear chirp (work to be published). Another way of systematically shaping the laser field is represented by femtosecond interferometry (*Chem. Phys. Lett.*, 2010, **487**, 209–213 and *J. Chem. Phys.*, 2008, **128**, 121104). The V-chirp (or lambda chirp), suggested by you, is yet another concept for systematically shaping fs-laser pulses. We have not performed experiments employing this concept yet, but will consider it in future work.

**Professor Whitaker** addressed Professor Field and Professor Weitzel: I would just like to add to Professor Field's question that some time ago we investigated chirp control of the (slightly off resonant) three photon pumping of an ion pair state in molecular iodine using visible light (N. T. Form, B. J. Whitaker and C. Meier, *J. Phys. B: At. Mol. Phys.*, 2008, **41**, 074011). Similarly to the results just presented by Professor Weitzel we also found that the transform limited pulse was a relatively inefficient means of pumping the target state and that higher efficiencies (by a factor of three or more) could be achieved by applying linear chirp. But we also investigated the effects of higher order chirp and made systematic maps (see the figure below) of the pumping efficiency as a function of group delay and third order dispersion (linear and quadratic chirp). We found that the addition of time ordering (quadratic chirp) to the excitation pulse had a significant extra enhancing effect. This was attributed to creating a double pulse temporal structure (an effect that could also be generated by applying a pi-phase flip in the middle of the excitation spectrum) which we showed was effective through a time delayed resonance in which the first pulse created population on an intermediate state which then had to propagate (as wavepacket) to larger interatomic distances before it could be efficiently transferred to the final state by the second temporal component. The fact that in ethane no effect is observed for third order dispersion may indicate that here the



**Fig. 1** Pumping efficiency as a function of group delay and third order dispersion.

fragmentation channels are reached by a final photon only connecting two states through a wavepacket following mechanism.

**Professor Reid** communicated: Do you have any physical insight into why changing the sign of the chirp changes the branching ratio of the photofragments?

**Professor Weitzel** communicated in reply: Clearly a profound answer would require a thorough theoretical calculation taking into account both ionization dynamics as well as wavepacket dynamics (for the nuclei and for the electrons). We are not in the position to provide this. Thus we can only offer qualitative arguments. In the dissociative ionization of DCl we observed that the formation of  $\text{Cl}^+$  from the electronic ground state potential of the ion was favored over the formation of  $\text{D}^+$  from the first excited electronic state of the ion for the application of negative linear chirp, but not for positive linear chirp. We interpreted this as an indication that climbing the anharmonic ladder of vibrational states is favored by a negative linear chirp (*J. Chem. Phys. A*, 2006, **110**, 6395–6398). On the other hand theoretical wavepacket work suggested that in addition to vibrational ladder climbing effects also electronic resonances can become important. Here, we recall that the energetic distance between electronic states in general depends on the reaction coordinate (in particular for bound-free transitions) and consequently may change during the chemical process of interest. To our knowledge there is no unique answer as to when the "jump" to another electronic state is favored by negative or positive chirp.

**Professor Duxbury** communicated: In Figure 8, ion yields from d3 ethane, one curve stands out as having a much larger ion yield over a longer time period than the other 5 examples, it would be interesting to have an explanation for this.

In 2011, in the Faraday Discussion 150, Frontiers of Spectroscopy, Oka gave an interesting introduction on "Spectroscopy and astronomy:  $\text{H}_3^+$  from the laboratory to the Galactic center. In Figure 11 of this discussion The observed spectra lines observed go well above the barrier to linearity well into the visible region. It would be interesting to reconcile the behaviour of the triatomic ions which your group is studying with the highly excited  $\text{H}_3^+$  ions produced by a very different series of methods.

**Professor Weitzel** communicated in reply: The particular ion exhibiting the largest yield for the shortest pulse duration up to about 120 fs pulse duration is the parent ion. The data shown in Fig. 8 reflects the fact that the ratio of all fragment ions to parent ions increases with increasing negative chirp value (see also Fig. 4) This again supports our interpretation that ionization is followed by dissociation. As I discuss in my general discussion of papers 18–20 the photo-dissociation of  $\text{H}_3^+$  leading to the formation of  $\text{H}_2^+ + \text{H}$  has been observed experimentally (Bae and Cosby, *Phys. Rev. A*, 1990, **41**, 1741). The threshold for observing  $\text{H}_2^+$  was around 2.5 eV (!). Since the dissociation energy is about 4.9 eV this immediately implied that the  $\text{H}_3^+$  ions were rovibrationally hot, presumably above the barrier for linearity you are referring to. This barrier for linearity lies at  $9913\text{ cm}^{-1}$  (the same source as the one you quote). Now the interesting question is, whether one will be able to photoinduce the formation of  $\text{H}^+ + \text{H}_2$  on the electronic ground state potential. The dissociation limit of the latter is 2 eV below that for  $\text{H}_2^+$  formation.

**Professor Meier** asked: The yield of all ions seems to be favoured by a negative chirp. Is this an indication that the chirp effect occurs on the very first ionisation step ?

**Professor Weitzel** replied: There is most likely more than one chirp effect in this work. Quite obviously there is a chirp effect on the formation of the parent ion, thus in the first ionisation step. But there are also chirp effects in what we call inter-charge-state-control (control between fragments originating from the monocation and from the dication) and intra-charge-state-control (control between fragments originating from the same charge state).

**Professor Whitaker** commented: If we think back to Gustav Gerber's early evolutionary control experiments, *e.g.* M. Bergt, T. Brixner, B. Kiefer, M. Strehle and G. Gerber, *J. Phys. Chem. A*, 1999, **103**, 10381, the usual way to provide a feedback signal to the control loop is to monitor two or more ion products, because ions are easy to detect, and to generate a fitness parameter from the ratio of the signals, much as in your experiments. Although clear control was demonstrated, the mechanism in polyatomic molecules was as clear as mud. A particularly striking example was the experiment by Levis and coworkers (R. J. Levis, G. M. Menkir and Herschel Rabitz, *Science*, 2001, **292**, 709) in which they observed the formation of toluene and carbon monoxide (ions) with highly structured electric fields centred around 800 nm applied to acetophenone. If the dynamics occurred on excited state surfaces of the neutral molecule this would be a remarkable result (requiring as it does the concerted breaking of two bonds and the formation of a third). It seems much more likely that the dynamics are in fact occurring on the ionic surfaces, similarly to McLafferty rearrangement reactions. Since at least 4 or 5 near IR photons are required to ionize ethane do your chirp results (which implicitly imply some kind of wavepacket following mechanism between two near resonantly coupled surfaces) not strongly suggest that in your results too it is the ionic PESs that play the crucial role in directing the fragmentation patterns?

**Professor Weitzel** commented in reply: As we tried to demonstrate by kinetic energy analysis the fragment ions discussed in the current work are mainly formed on the dicationic potential energy surface (PES), some on the monocationic PES, thus implying an "ionization followed by dissociation" mechanism.

**Professor Meier** communicated: What are the challenges, from a theoretical point of view, to fully simulate the observed chirp and intensity dependent results?

**Professor Weitzel** communicated in reply: The main theoretical challenge for simulating experiments of this kind (starting from the neutral molecule) from my point of view is that you need to combine state-of-the-art theory for ionization dynamics with state-of-the-art theory for dissociation dynamics. We have done both separately, *e.g.* Korolkov and Weitzel, *Chem. Phys. Lett.*, 2010, **487**, 209–213, for the dissociation dynamics and Znakovskaya *et al.*, *PCCP*, 2011, **13**, 8653–8658, for ionization dynamics, but not combined in one calculation. The combination of the two is currently perhaps only tractable for molecular hydrogen and a few

other small molecules. There is an intriguing advantage of looking at the photodissociation dynamics of the ion in the first place. Typically the next higher charge-state is energetically far away. Thus, you do not have to worry about that. The separation of electronic states in the ion (mono-cation) is typically smaller than in the neutral. In the end, this is the reason, why I have suggested the  $\text{H}_3^+$  experiment (see the general comment below).

**Professor Weitzel** communicated: A general comment in the discussion of papers 18–20. The  $\text{H}_3^+$  ions, the formation of which we describe in our paper, is not only intriguing because it involves the breaking of three C–H bonds and the formation of three H–H bonds (it's a cyclic species). It is most of all the top molecular system for studying the possibilities and the limits of photochemical control schemes. There are several reasons for this claim:

i) There is no neutral analogue to the  $\text{H}_3^+$  ion. Thus, the photodynamics of this system can be investigated free from any contamination of neutrals.

ii) The  $\text{H}_3^+$  ion has two dissociation limits, the formation of  $\text{H}_2^+ + \text{H}$  and the formation of  $\text{H}^+ + \text{H}_2$ . These two limits are separated by about 2 eV (the difference in I.E.s of  $\text{H}_2$  and H). I would like to suggest attempting to control the yields of these two reaction channels by applying any of the experimental control schemes currently available to  $\text{H}_3^+$  ions prepared in an ion trap.

iii) The  $\text{H}_3^+$  ion consists of three protons and two electrons. It is the smallest molecular system for which we can envisage the competition between two reaction channels easily distinguishable in any mass spectrometer. It appears conceivable to test the experimental data against the highest levels of theory available to date.

**Professor Whitaker** communicated in reply: It's known that the vertical excitation energy from the  $(1)^1\text{A}'$  to  $(2)^1\text{A}'$  state in  $\text{H}_3^+$  is 20 eV or so. The latter state, which correlates with the  $\text{H}_2^+$  plus H dissociation channel, is purely dissociative and never crosses the ground state. So I'm not sure that I understand your proposed experiment. How will it be possible to control the branching ratio between the  $\text{H}_2$  and  $\text{H}_2^+$  channels?

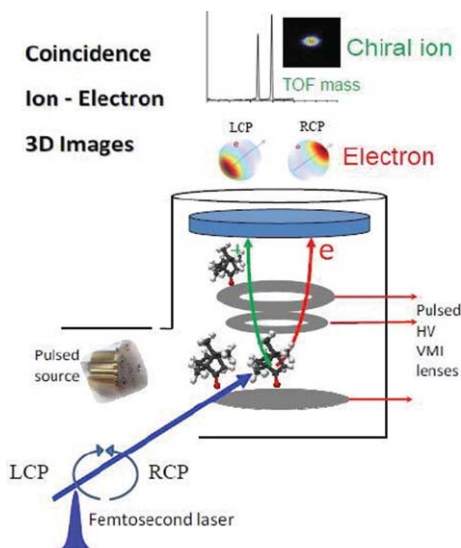
**Professor Weitzel** commented further: One does not have to rely on the vertical excitation from the rovibrational ground state of  $\text{H}_3^+$   $(1)^1\text{A}'$  all the way to the  $(2)^1\text{A}'$  state. The photodissociation of  $\text{H}_3^+$  has been described *e.g.* by Bae and Cosby in 1990 (Y. K. Bae and P. C. Cosby, *Physical Review A*, 1990, **41**, 1741) above 2.5 eV starting from hot  $\text{H}_3^+$ . More recent work is by Petriniani *et al.*, *Journal of Physical Chemistry*, 2010, **114**, 4864. I am convinced that chirped pulse excitation of cold  $\text{H}_3^+$  will eventually bring you to the same "region", where one or two additional photons at 800 nm can decide between the  $\text{H}_2^+$  and the  $\text{H}^+$  channel. I would speculate that down chirp leads may lead to  $\text{H}^+$  on the ground state surface, and up chirp leads may lead to  $\text{H}_2^+$  by jumping to the upper surface (in the last moment). We believe we have seen something similar in HCl (H. G. Breunig, A. Lauer, and K. M. Weitzel, *Journal of Physical Chemistry A*, 2006, **110**, 6395), however there we started from the neutral, and we were not able to prove that the control is in the ion. That would be the advantage of the  $\text{H}_3^+$  experiment.



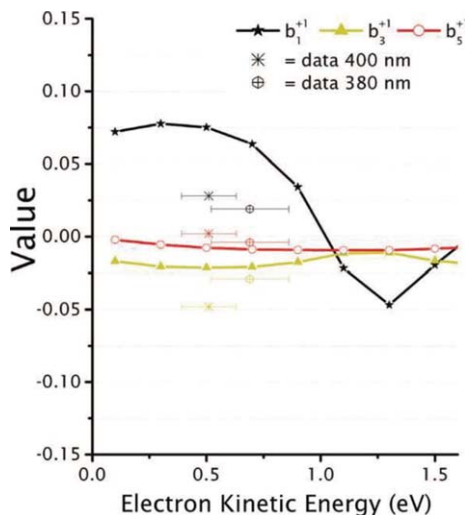
**Professor Whitaker** responded: Thank you for the clarification, but given that the energetic gap between the (1)  $^1A'$  to (2)  $^1A'$  states converges along the dissociation co-ordinate perhaps a down chirped pulse might be more successful in promoting the molecular ion channel. I look forward to someone trying the experiment to see who is right!

**Mr Lehmann** asked: As a question addressed to Professor Weitzel, we would like to ask the following. Do you think that it would be useful for the interpretation of your chirped pulse shaping experiments on ethane, and similar molecules, at these fluence levels of about  $10^{13}$  Watt/cm<sup>2</sup> to extent the ion-TOF data with more advanced three-dimensional momentum imaging, and in particular to combine this with coincidence electron imaging?<sup>1,2</sup>

In this respect we (C. S. Lehmann, N. B. Ram, I. Powis and M. H. M. Janssen) would like to provide the following comment. Recently, we have introduced a novel technique, multi-photon photoelectron circular dichroism (MP-PECD) to discriminate the enantiomers of chiral molecules with mass-selectivity using photoelectron-photoion coincidence imaging [Fig. 2 and Ref. 3,4]. We employ femtosecond multi-photon ionization with circular polarized light and depending on the wavelength and laser fluence we also observe ion fragmentation.<sup>4</sup> The forward-backward asymmetry in the angular distribution of photoelectrons is measured in coincidence with an ion. The coincidence technique makes it possible to measure and analyse this asymmetry in correlation with the observed mass of the ion. Furthermore, the photoelectron spectra measured provide information about the mechanism that leads to the various fragmentation channels. For the chiral molecule Camphor, the asymmetry observed for excitation near 400 nm is 8%.<sup>3</sup> Because the ionization is due to a three-photon excitation we can expand the angular asymmetry in Legendre polynomials up to order



**Fig. 2** Schematic illustration of the coincident measurement of the forward-backward asymmetry in the electron distribution from femtosecond multi-photon ionization of a chiral molecule with circular polarized light.



**Fig. 3** Comparison of the measured and calculated odd Legendre moments of the electron angular distribution of Camphor.<sup>4</sup>

six. In collaboration with Professor Powis we have attempted to get a better theoretical understanding of the mechanism and the magnitude of the Multi Photon PECD effect.<sup>4</sup> The calculated Legendre coefficients of the photoelectron angular distribution parameters ( $b_1 - b_6$ ), see Fig. 3, can be compared with the experimental values. It is very encouraging that there is good qualitative agreement regarding the sign of the coefficients and to some extent quantitative agreement. Further theoretical work is in progress, as well as experiments on other molecules.

1. C. S. Lehmann, N. B. Ram, D. Irimia and M. H. M. Janssen, *Faraday Discussions*, 2011, **153**, 173.
2. C. S. Lehmann, N. B. Ram and M. H. M. Janssen, *Rev. Sci. Instrum.*, 2012, **83**, 093103.
3. N. B. Ram, C. S. Lehmann and M. H. M. Janssen, *European Physical Journal, Web of Conferences*, 2013, **41**, 02029.
4. C. S. Lehmann, PhD Thesis, VU University Amsterdam, ISBN 978-90-6464-660-7 (2013).

**Professor Weitzel** replied: I agree that coincidence studies may add to a better understanding of the ionization /dissociation dynamics. In fact, there was a time when I was concentrating on electron-ion-coincidence experiments, which finally led to my Habilitation (K.-M. Weitzel, "Energetik, Kinetik, und Mechanismus von unimolekularen Elementarreaktionen in Molekül- und Cluster-Ionen." Shaker-Verlag, 1998, Aachen, ISBN 3-8265-3376-3). More recently we have employed the ion-ion-coincidence imaging technique to improve our understanding of the ethane dication dissociation (Kanya *et al.*, *J. Chem. Phys.*, 2012, **136**, 204309). We certainly would like to continue performing coincidence imaging experiments in the future. However I would like to comment on the relation of imaging experiments *versus* straight time-of-flight measurements: the latter will normally provide a higher kinetic energy resolution. This holds true for the ions as well as for the electrons. It depends on your scientific question whether the imaging or the ToF concept is preferable.

I am pleased to finally see the measurement of a circular dichroism in the photoelectron angular distribution (PECD /PAD) in coincidence with the ion signal. As you know, we have (again) concentrated on the ion in related studies. To the best of my knowledge we were the first to demonstrate the measurement of a circular dichroism in femtosecond laser ionization of a chiral molecule four years ago (Breunig *et al.*, *ChemPhysChem*, 2009, 8, 1199–1202). While our CD effect originated mainly from the magnetic dipole transition moment, the PECD effect you show is electrically dipole allowed. It would be intriguing if you could perform an experiment on the 3-methyl-cyclopentanone around 310 nm, where we have observed CD values as large as 15% in total ion yields (angle integrated!). Your experiment should then demonstrate whether the contributions from the different transition moments add up. Finally I would like to point out that in my view the prospect for applying femtosecond laser pulses for chirality analysis is in the non-resonant ionization, since there you can detect any molecule. Again we were the first to demonstrate the viability of this concept (Horsch *et al.*, *Chirality*, 2012, 24, 684–690). Here, my question would be, will it be possible to extend your fs-PECD measurement to the non-resonant multi-photon-ionization, where we talk about 8 photons or more, or will your PECD effect be killed by the higher order Legendre polynomials?

**Mr Lehmann** communicated: We (C. S. Lehmann and M. H. M. Janssen) would like to address the following question to Professor Weitzel. In Fig. 2, 3 you show that the influence of the linear chirp is not symmetric, but that only negative chirp enhances the fragmentation. Therefore, it is concluded that it is not a time duration effect that is responsible for the fragmentation dynamics. In our group in Amsterdam we have reported previously pulse shaping studies in combination with electron and ion imaging detection.<sup>1,2</sup> In these experiments we used femtosecond multi-photon excitation at visible wavelengths around 520 nm. However, we observed that the effects of, for instance chirp on fragmentation dynamics in molecules like CF<sub>3</sub>I and CH<sub>2</sub>BrCl, were very dependent on the central wavelength. In Table 1 we have summarized some more recent data measured with our coincidence set-up at 2 different wavelengths and quite different effects are observed regarding the effect of chirp on the fragmentation ratios. Do you think that your results on ethane are dependent on the exact central wavelength

**Table 1** Single color multi-photon ionization of CH<sub>2</sub>BrCl. The laser pulses (repetition rate 1 kHz) were centered at 521 and 526 nm, had a bandwidth of 20 nm and a pulse energy of 10 μJ. Experimental data by C. S. Lehmann and M. H. M. Janssen (unpublished results Amsterdam).

	$\phi'' = -200 \text{ fs}^2$	$\phi'' = 0 \text{ fs}^2$	$\phi'' = +200 \text{ fs}^2$	$\phi'' = +400 \text{ fs}^2$
<b>521 nm</b>				
Total ions (per sec)	0.81	4.63	3.63	0.49
CH <sub>2</sub> Cl <sup>+</sup> /CH <sub>2</sub> BrCl <sup>+</sup>	0.34	0.37	0.51	0.65
CH <sub>2</sub> Cl <sup>+</sup> /all ions	0.71	0.68	0.62	0.57
CH <sub>2</sub> BrCl <sup>+</sup> /all ions	0.24	0.25	0.32	0.37
<b>526 nm</b>				
Total ions (per sec)	2.48	4.04	3.94	1.94
CH <sub>2</sub> Cl <sup>+</sup> /CH <sub>2</sub> BrCl <sup>+</sup>	0.34	0.33	0.36	0.41
CH <sub>2</sub> Cl <sup>+</sup> /all ions	0.24	0.23	0.25	0.28
CH <sub>2</sub> BrCl <sup>+</sup> /all ions	0.70	0.71	0.70	0.68

used, and would it be useful to change the central wavelength to other wavelengths and measure the effect of the linear chirp? Do you expect changes with wavelength?

1. D. Irimia, and M. H. M. Janssen, *J. Chem. Phys.*, 2010, **132**, 234302.
2. C. S. Lehmann, N. B. Ram, D. Irimia and M. H. M. Janssen, *Faraday Discussions*, 2011, **153**, 173

**Professor Weitzel** communicated in reply: Your CF<sub>3</sub>I experiments performed between 520 nm and 550 nm are basically two-photon resonant with the first electronically excited A state, compare *e.g. J. Chem. Soc., Faraday Trans.*, 1997, **93**, 2839–2846. You are probably influenced by several additional resonances at the three photon level and higher. Most likely all your very interesting observations are the result of resonances and moreover interferences between resonances. The situation may be very similar for the CH<sub>2</sub>BrCl. The situation is fundamentally different for the current ethane study, where the first very weak optical absorption is centered at 8.7 eV (143 nm) and the first strong absorption occurs at about 9.4 eV (132 nm), see *Chemical Physics*, 1993, **173**, 209–239. Our experiment has been performed at 800 nm. Thus it would take 6 photons to reach the first excited electronic state in a resonance picture. Very likely the fs-laser ionization of ethane at 800 nm is non-resonant. Changing the wavelength is not expected to alter our observations.

**Professor Burgdoerfer** opened the discussion of the paper by Professor Bucksbaum by communicating: You discussed two somewhat complementary models for the enhanced multiple ionization near conical intersections. Would it be possible to distinguish between the two, for example by varying the frequency?

**Professor Bucksbaum** communicated in reply: Yes, varying the frequency might reveal valuable distinguishing characteristics. We already pointed out that a feature of the conical intersection region is a “resonant ring” surrounding the singularity in the g-h plane. The laser frequency controls the size and shape of this ring. An equally important question in the case of double ionization is whether the cation *also* contains a conical intersection or resonances in the vicinity that could facilitate removal of the second electron.

**Dr Kirrander** communicated: Your observation of enhanced multiple ionization near conical intersections is intriguing: High harmonic generation (HHG) spectroscopy is being actively explored as a tool for studying molecular dynamics in the vicinity of conical intersections<sup>1</sup>. Crucially, the HHG process relies on *single* electron ionization and recombination. If enhanced *multiple* ionization is a common feature at conical intersections, do you believe it will constitute a problem for this otherwise promising set of techniques?

Also, do you have any plans to examine the reported phenomenon in simpler molecules, where it may be easier to characterize the states and the structure of the molecule at the conical intersection?

1. H. J. Wörner, J. B. Bertrand, B. Fabre, J. Higuët, H. Ruf, A. Dubrouil, S. Patchkovskii, M. Spanner, Y. Mairesse, V. Blanchet, E. Mevel, E. Constant, P. B. Corkum, and D. M. Villeneuve, *Science*, 2011, **334**, 208–212.

**Professor Bucksbaum** communicated in reply: Dr Kirrander has identified some important questions regarding the implications of our results. If multiple ionization occurs, this may suppress HHG, both through poorer phase matching effects in the resulting plasma and by limiting the neutral recombination probability for the molecule. Future experiments will investigate this possibility. We do have plans to pursue this research with simpler molecules. Even diatomic molecules, which do not have conical intersections, might have enhanced multiple ionization if the enhancement is aided by laser-induced resonant phenomena.

**Professor Stolow** communicated: Great progress in strong field ionization (SFI) obtained from use of the quasi-static approximation wherein a single driven electron responds adiabatically to the applied field, allowing development of a well known tunnelling picture of SFI. This simple model has worked exceedingly well in atomic physics, giving birth to the entire field of Attosecond Science. However, the interaction of strong laser fields with polyatomic molecules can be a complicated situation in which both the adiabatic<sup>1,2</sup> and single active electron approximations<sup>3,4</sup> can fail dramatically. The latter can be somewhat naively thought of as a consequence of the non-zero low frequency polarizability of the core (*i.e.* dynamic screening). The former, the failure of the adiabatic approximation, is a consequence of inverse electronic level spacings being comparable to time scale of the strong field dipole coupling. These two situations are not wholly independent, as the polarizability (a derived quantity) is a sum over dipole matrix elements divided by electronic energy level spacings. In situations where these approximations fail, it has been shown that multiple ionization and extensive fragmentation of polyatomic molecules can result.<sup>1</sup>

In a dynamic, photoinduced process such as passage through a conical intersection, I would expect that both electronic level spacing and polarizabilities would vary as a function of internal vibrational coordinates. A conical intersection is, in essence, a 'transition state' in an electronically excited state rather than the ground state. In ground state reaction dynamics, I would expect the 'transition state' to be a point of maximum polarizability. Intuitively, this could be understood from the fact that, at the 'transition state', the valence electrons are most delocalized, being by definition somewhere between the old bonds and the new ones. A bit more quantitatively, barriers on ground state potential energy surfaces often arise from very strongly avoided crossings with far away electronically excited states. In this situation, the relevant excited state will have a minimum at geometries corresponding to that of the ground state transition state.

The strong variation of both polarizabilities and electronic level spacing near conical intersections could have important consequences for SFI. Particularly relevant is that the SFI molecular response could change from adiabatic to non-adiabatic upon passage through a conical intersection. The consequences of this could certainly be enhanced ionization and fragmentation.<sup>1</sup> I propose that the variation of the SFI response seen in your results may be due to such effects. If this can be confirmed, then I would say that this method could be used to perhaps locate or determine passage through conical intersections.

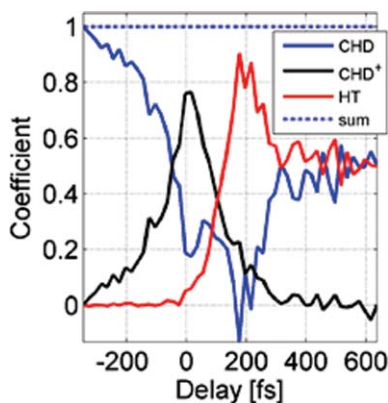
1. M. Lezius, V. Blanchet, M. Yu. Ivanov and A. Stolow, Polyatomic molecules in strong laser fields: Nonadiabatic multielectron dynamics, *Journal of Chemical Physics*, 2002, **117**, 1575.
2. M. Lezius, V. Blanchet, D. M. Rayner, D. M. Villeneuve, A. Stolow and M. Yu. Ivanov, Non-adiabatic multi-electron dynamics in strong field molecular ionization, *Physical Review Letters*, 2001, **86**, 51.

3. M. Smits, C. A. de Lange, A. Stolow and D. M. Rayner, Absolute ionization rates of multi-electron transition metal atoms in strong infrared laser fields, *Physical Review Letters*, 2004, **93**, 213003.
4. M. Smits, C. A. de Lange, A. Stolow and D. M. Rayner, Dynamic polarization in the strong field ionization of small metal clusters, *Physical Review Letters*, 2004, **93**, 203402

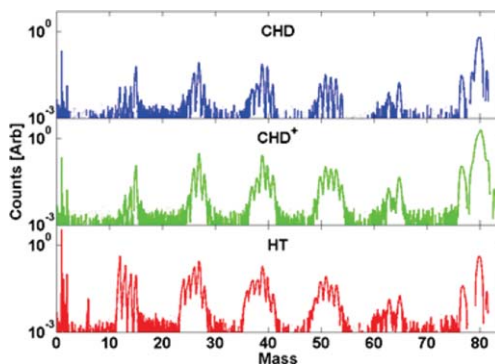
**Professor Neumark** asked: Can you elaborate on the data in Fig. 2? In particular, how do you use mass spectroscopy to distinguish among the three species responsible for the curves in Fig. 2 given that all three have the same parent mass?

**Professor Bucksbaum** responded: Here Professor Neumark is referring to the following figure:

This figure, as described in the caption, is from the paper of White *et al.* [J. L. White, J. Kim, V. S. Petrović and P. H. Bucksbaum, *The Journal of Chemical Physics*, 2012, **136**, 054303]. The White paper uses the method of spectral unmixing to discover the linearly independent mass spectral signatures of each of the three channels, corresponding to fragmentation of CHD, CHD<sup>+</sup>, and HT in the figure.



**Fig. 4** Relative abundance of the mass fragment TOF spectral signatures associated with CHD and HT following photoexcitation. Reprinted from White *et al.*, with permission.



**Fig. 5** Spectral amplitudes of the data projected into the three dimensional subspace. Reprinted from White *et al.*, with permission.

Although these species all have the same mass, their fragmentation patterns are quite distinct. Here is another figure from White *et al.* that shows that:

These so-called “endmember” spectra represent the best approximation from the data of the pure spectral signatures of the three species. Then the data are projected into the three dimensional subspace of these three channels, and the spectral amplitudes of these projections are depicted in the figure.

**Professor Domcke** communicated: There are various ways how quasidegeneracies of potential-energy surfaces can arise in polyatomic molecules. What is unique about conical intersections is the Longuet-Higgins phase, also known as the Berry phase. Does this phase play a role in your double-ionization mechanism *via* conical intersections?

**Professor Bucksbaum** communicated in reply: The data presented here do not help to answer this question, so I can only speculate about it. Double ionization suggests either ionization energy suppression or intermediate resonances in the cation states of the molecule in this geometry, and of course the Berry phase is also a manifestation of topology. If the geometry-induced CI energy degeneracy between pairs of states with different symmetry persists in both the neutral and the cation, then enhanced ionization through the dipole interaction of these two states might also be present in both. I stress that this is only speculation, but calculations of the location of the CI seams in the cation might help support this line of reasoning.

**Dr Mendive-Tapia** opened the discussion of the paper by Professor Brumer: Besides the expressions derived for the density matrix, I was wondering if you have searched for further insights by looking at relaxation time-dependent rate constants. As said in the last sentence of the paper, this could be done numerically for individual systems, or perhaps in a complementary way, analytically for a specific form of the Hamiltonian (*i.e.* linear vibronic coupling Hamiltonian).<sup>1–6</sup>

1. M. H. Cho, R. J. Silbey, *J. Chem. Phys.*, 1995, **103**, 595.
2. R. D. Coalson, D. G. Evans, A. Nitzan, *J. Chem. Phys.*, 1994, **101**, 436.
3. A. F. Izmaylov, D. Mendive-Tapia, M. J. Bearpark, M. A. Robb, J. C. Tully, M. J. Frisch, *J. Chem. Phys.* 2011, 135.
4. S. Jang, Y. J. Jung, R. J. Silbey, *J. Chem. Phys.*, 2002, **275**, 319.
5. S. Mukamel, V. Rupasov, *Chem. Phys. Lett.* 1995, **242**, 17.
6. E. Neria, A. Nitzan, *J. Chem. Phys.*, 1993, **99**, 1109.

**Professor Brumer** communicated in reply: Dr Leonardo Pachon and I have indeed examined this in greater detail in order to gain insight into the origins of the phase control, and its possible magnitude.

Rather than using the approaches that you suggest, we studied a exactly soluble model using an exact influence functional method. Results will be submitted shortly for publication.

**Professor Meier** enquired: In a publication by M. Joffre (*Science*, 2007, **317**, 453b), very general rules on when a phase control should or should not be present are established. In the examples shown when a one-photon control is observed, which of his general rules are violated in the different cases ?



**Professor Brumer** communicated in reply: As you know, Miller and co-workers addressed this issue in a reply to the Joffe comment. They suggested that the difficulty with his argument related to the issue of time translation symmetry. Further, do note that a subsequent analysis of the general situation [Spanner, Arango and Brumer, *J. Chem. Phys.*, 2010, **133**, 151101] we showed that phase control is allowed for the measurement of observables that do not commute with the system Hamiltonian. This is indeed the case for the property that Miller *et al.* measured, *i.e.* the control of isomerization. In this case the environment is necessary in order to prevent the system from going periodically between the *cis* and the *trans* configurations. However, it is not necessary for phase control to be permitted. Indeed, we recently demonstrated [Arango and Brumer, *J. Chem. Phys.*, 2013, **139**, 071104] one-photon phase control in a multidimensional model of retinal in rhodopsin, a case related to the original experiment.

**Dr Santoro** communicated: I really enjoyed reading your elegant paper and I think that the establishment of a formal condition that indicates when a one-photon phase control is possible is a very nice result. You state in the introduction that in a closed system one can achieve a one-photon phase control when the observable one tries to control does not commute with the molecular Hamiltonian. Control of a photoisomerization is possible since the probability to find the system in one of the two isomers does not commute with the Hamiltonian. In other terms, if I understand properly, the control is possible because the vibrational states in the *cis* and *trans* wells of the potential energy surface (PES) are not eigenstates of the molecular Hamiltonian. To fix the ideas, let us say that at time  $t = 0$  we know that the system is in the *cis* isomer. This also means, if I am correct, that one can create an excess of population of the *trans* isomer at a given time but, waiting for a sufficiently long period, the system will be back in the *cis* isomer, if it is completely isolated. In my understanding, in all practical cases this does not happen because interaction with the environment introduces dephasing mechanisms, so that the population of the *trans* isomer does not revert spontaneously to zero. Maybe this question is a bit philosophical but: can therefore we say that also in the case of an isolated system one needs to take into account the coupling with an “environment” to explain why the population of the reaction product is permanent? Probably everything rings around the definition of “system” and “environment” but, if the role of the “environment” is played by a bath of secondary modes of the system itself, does this conceptually change the picture? In an open system it is possible to control also an observable that commutes with the system Hamiltonian and, as you clearly state in Ref. 1, this is connected with the fact that the observable does not commute with the Hamiltonian of the “super-system” comprising the system and the environment. These considerations help me to introduce the following very qualitative questions:

(i) can we say that one of the results of your work is that in most of the problems of chemical interest one-photon phase control is possible because the system will always interact with an environment?

(ii) any computational simulation of a control experiment adopts a model of the real system, neglecting therefore some parts that can play the role of an “environment”. In this context, does your work in some sense support the idea that a control scheme able to focus, at a given time, a large excess of population in a desired reaction channel, or in a isomer well (even if this is a transient

population for the “isolated model system”) can provide an effective route for control, if chemical intuition suggests that interaction with the neglected environment will make the “reaction” not reversible?

Clearly your analysis allows getting a much deeper understanding of the control mechanism. For example you show that the environment-assisted control acts on two different timescales, the timescale of the radiation field and the timescale of the system-bath interaction. Is it possible to make some general, qualitative, statement on which of the two timescales is expected to be more “crucial” for the control?

1. M. Spanner, C. A. Arango and P. Brumer, *J. Chem. Phys.*, 2010, **133**, 151101.

**Professor Brumer** communicated in reply: My co-author, Leonardo Pachon, and I appreciate your questions and answer them below.

Control over isomerization in an isolated molecule is indeed possible since the probability of finding the system in one of the two isomers (e.g., *cis* or *trans*) is an observable that does not commute with the molecular Hamiltonian. However, as pointed out in the question, if one waits long enough, the a flow back of population should be observed, and it is in this particular aspect that the environment plays a major role, i.e. in “stabilizing the product”.

In the case where “environment” is comprised of secondary modes of the system itself, we break the time reversal symmetry over an effective time scale which depends upon the dimensionality of the “environment”. According to the Poincare recurrence theorem, that time scale grows exponentially with the number of degrees of freedom of the system. In the case discussed in retinal isomerization by Arango and Brumer, *J. Chem. Phys.*, 2013, **138**, 071104, the 24 modes of vibration of the system are able to prevent, on an effective time scale, the back and forth transfer of population between *cis* and *trans*.

Your comment that phase control should then be possible for most of problems of chemical interest since the system will always interact with an environment, is correct. However, our general results show only the existence of that effect. The magnitude of the effect, as we discuss in the end of our paper, will depend on the nature of the system-environment interaction. In a forthcoming paper, we explore in a quantitative way the magnitude of that effect, showing that it depends on the field characteristics, such as strength and frequency, as well as on environment properties such as temperature and memory.

The next question asks whether our work supports the idea that a control scheme able to focus a large excess of population in a desired reaction channel can provide an effective route to control, if chemical intuition suggests that the interaction with the neglected environment will make a process non-reversible.

Our results do suggest this. However, we think that control of such a process could be challenging because it would imply the control over, in principle, several degree of freedoms. However, one could try to “engineer” the environment in order to get a desired result. For example, one could ask whether, e.g., coherently pumping the vibrational modes in order to transfer energy from one electronic freedom to another or to break an electronic bonding is a realistic approach. This could provide an alternative, indirect, means of environmentally assisted coherent control.

Finally, you ask if it is possible to make some general qualitative arguments as to which of the two time scales is expected to be more crucial for the control. Since one is interested in control in the long time regime, one expects that this limit is dictated by the system-environment interaction. Hence, we anticipate that the contribution taking place in the radiation field timescale, mediated by the off-diagonal elements, is less “crucial”, in the long time regime, than the contribution coming from the system-environment interaction itself. For a detailed study of a specific model we refer to a forthcoming publication by Pachon and Brumer.

**Miss Perveaux** opened the discussion of the paper by Dr Blancafort by communicating: When the external field is on, the second excited state comes very close to the states you are studying. You may thus want to include this second excited state in your model.

Do you know if your choice of active coordinates is suited to study this state or should you consider some other coordinates? Can you trust calculations at the CASSCF level of theory for this state, or do you need to include dynamic electron correlation?

**Dr Blancafort** communicated in reply: In our work we assume that the active coordinates derived for the field free situation are also suitable when the non-resonant field is active, in other words, we assume that the position of the critical points on the surface does not depend on the non-resonant field. One may question this assumption already for the first excited state and the ground state. However, we believe that the changes will be small, and since the present study is more of a proof of principle, we have not taken this into account yet. It is something that we will test in the future. Of course, if one wants to include more states in the dynamics, the number of relevant coordinates will increase because other regions of the surface may become relevant.

Regarding dynamic correlation, we know that CASSCF gives a good description of  $S_0$  and  $S_1$ , but we have not checked the importance of dynamic correlation for  $S_2$ .

**Professor Domcke** communicated: My question refers to Fig. 7 in your paper. While the oscillatory structure at short times is strongly affected by the control field, the long-time limit of the population of the V state seems not to be affected. What is the physical reason for this?

**Dr Blancafort** communicated in reply: This is due to the extended nature of the seam, and it is one of the punchlines of our work. Initially the decay follows the totally symmetric stretch coordinate, and the seam of intersection at planar geometries is energetically not accessible. After approximately 50 fs, intramolecular vibrational energy redistribution activates the torsional mode, and the region of the seam at twisted geometries can be accessed. Clearly, such an effect only appears if the extended nature of the seam is explicitly taken into account in the model.

**Dr Santoro** communicated: The decay of your system is ultrafast, so there is only a very short time-window to try to control it. You mention in fact that most of the photoexcited population returns to the ground state in less than 10 fs. I imagine therefore that you used an ultrashort resonant pump laser pulse in your

simulations, and this seems coherent with what is seen in Fig. 5 of your paper, where the excited state population rises in about 5 fs. Then you use a second dynamic non-resonant “control” field that oscillates with a period of 4 fs, assuming that it is switched on before the resonant one. In such a situation, does the control efficiency depend on the “phase” of the non-resonant field, or in other terms on the delay between the starting of the two fields?

**Dr Blancafort** communicated in reply: You're right, the time window to control the decay is very short, and therefore we consider it a success to be able to delay it by a few tens of femtoseconds. Regarding your question, it is an interesting point, since the duration of the resonant and non-resonant pulses is similar, as you point out. We will check the influence of the phase and the delay in future work.

**Mr Binder** asked: Usually, the Multiconfigurational Time-Dependent Hartree (MCTDH) formalism is quite robust, *i.e.* a moderate number of configurations in most cases yields an at least qualitatively correct result. However, in your work you employed an unusually high number of configurations. Was this high number necessary to catch the qualitatively correct dynamics of the system or did you opt for this high number *a priori* to avoid convergence assessment? Furthermore, can you give a rough estimate, when to find most (say = 95%) of the population back in the ground state?

**Dr Blancafort** replied: We employed a large number of single particle functions in the combined  $Q_{x1}/\varphi$  mode because the surface along the  $\varphi$  coordinate is very flat, and the wave packet spreads along that coordinate. This makes the large basis necessary.

Concerning the time required to transfer most of the population to the ground state, we cannot give an estimate with the present model, because more modes would be required to dissipate the vibrational energy and avoid the recrossings to the excited state.

**Professor Whitaker** communicated: When one looks at Fig. 3 in your paper, and the population decay traces in Fig. 5, there is a striking similarity with the pictures presented to describe Marcus theory on moving from the inverted to normal regions, and I wonder to what extent a laser dressed state resembles a solvent shift and what further analogies can be drawn.

**Dr Blancafort** communicated in reply: Yes, there is a clear analogy with the Marcus picture and the passage from the inverted to the normal region. The behaviour is also similar to what Fermi's golden rule would predict for internal conversion, since the fastest decay rate is observed when the overlap between the  $S_1$  vibrational level accessed during the excitation and the ground state degenerate level is optimized.

In a first approximation, the laser dressed state resembles a solvent shift because both ‘environments’ (if we consider the non-resonant pulse as such an environment) act on the dipole moment of the molecule. However one should note that the laser induced shift depends more on the polarizability than on the dipole moment.

**Dr Malhado** addressed Professor Whitaker and Dr Blancafort: Since Professor Whitaker raised the question about possible analogies with the role of solvent polarity in this type of non-adiabatic processes, I would like to mention how in the context of a simple model<sup>1–3</sup> it is possible to show the important effect of a polar solvent on the potential energy surfaces, changing the position and topography of the conical intersection seam and inducing different reaction paths and product yields, in a very similar way to the effect of the applied external field shown in Dr Blancafort's article. Because upon electronic excitation the surrounding solvent is out of equilibrium with the solute charge distribution, I would like to highlight the importance of the solvent dynamics in such processes, as it occurs in a similar time scale as these ultra-fast reactions, and the above mentioned calculations indicate that different solvent dynamics *alone* can lead to different product yields. While the active control of the solvent environment does not seem *a priori* the simplest way to determine the outcome of a chemical reaction, in the context of "passive control" discussed at this conference, it has been known by chemists throughout history the importance of choosing the right solvent to optimize a certain product yield.

1. I. Burghardt, L. S. Cederbaum, J. T. Hynes, *Faraday Discuss.*, 2004, **127**, 395–411.
2. J. P. Malhado, J. T. Hynes, *J. Chem. Phys.*, 2012, **137**, 22A543.
3. J. P. Malhado, R. Spezia, J. T. Hynes, *Int. J. Quantum Chem.*, 2013, **113**, 296–305.

**Dr Blancafort** communicated in reply: Clearly, the position and topography of the seam are very important for the photochemistry, and I agree that the described solvent effects are a nice analogy to the non-resonant electric field effect.

**Dr Santoro** communicated: You mentioned that the solvent can control a nonadiabatic process altering the position and energy of a conical intersection (similarly to what an external field can do). I would like to add that this is exactly what, in our opinion, happens in nucleobases. Considering the  $\pi\pi^* \rightarrow n\pi^*$  internal conversion in uracil derivatives, our results<sup>1</sup> suggest that, moving from acetonitrile to water, the destabilization of the  $n\pi^*$  due to the loss of an hydrogen bond causes a shift of the conical intersection with the  $\pi\pi^*$  state, making it accessible or not from the Franck Condon region, depending on the substituent in position 5.

1. R. Improta, V. Barone, A. Lami and F. Santoro, *J. Phys. Chem. B*, 2009, **113**, 14491.

**Professor Duxbury** opened further discussion of the paper by Professor Bucksbaum by communicating: In neutral and ionised open shell triatomic molecules there are many examples of unusual intersections where three states are involved, and where two states are degenerate when the triatomic molecule becomes linear. Three series of molecules where this occurs are the  $\text{CH}_2$ ,  $\text{SiH}_2$ ,  $\text{GeH}_2$  family, the  $\text{NH}_2$ ,  $\text{PH}_2$ ,  $\text{AsH}_2$  family, and the  $\text{H}_2\text{O}^+$ ,  $\text{H}_2\text{S}^+$  and  $\text{H}_2\text{Se}^+$  family. The states which become degenerate when linear are a Renner–Teller pair, for example the A1 and B1 States of  $\text{CH}_2$ , and the other interacting state is triplet  $\text{CH}_2$ . The triplet state of  $\text{CH}_2$  can only interact with the lower singlet state of the pair of singlet states *via* an electronic Coriolis coupling between the Renner–Teller pair. As one proceeds from the first row of the periodic table to the second row the

atomic spin-orbit constant of the heavy atom becomes much larger, and pre-dissociation may occur so that breaking off of emission can occur, as in the hydrogen sulphide ion, or rapidly increasing broadening, as in  $\text{AsH}_2$ .

Although these are not strictly conical intersections, these effects do occur in some of the most commonly occurring small molecules, for example ionised water. They have also been studied by velocity map imaging, such as  $\text{H}_2\text{S}^+$  by Mike Ashfold and his group. There have also been doubly ionised examples such as those studied by John Eland.

**Professor Bucksbaum** communicated in reply: Professor Duxbury brings up an interesting point. Excited systems such as the A1 excited state in the water ion undergo rapid bending distortion and become degenerate with the ionic ground state as the molecule becomes linear. This is a degeneracy, but not a conical intersection. Therefore a fragmentation study of this molecule could shed some light on the necessary conditions for enhanced multiple ionization.

**Professor Weitzel** communicated: You have described an intriguing analysis of enhanced multiple ionization near conical intersections. Can you possibly relate your findings to the observation that multiple ionization in chirped femtosecond laser fields is capable of imaging local electron density onto fragment formation in a way which is very sensitive to structural isomerism (see *e.g.* G. Urbasch, H.G. Breunig, K.-M. Weitzel, *ChemPhysChem*, 2007, **8**, 2185–2188)?

**Professor Bucksbaum** communicated in reply: Professor Weitzel here refers to the paper by Urbasch *et al.*, which reported that the presence of  $\text{C}^{2+}$  in the photofragmentation spectrum of xylenes could be a high-contrast indicator of the isomer present. In particular, for the right pulse energies and chirp, para-xylene fragments included distinct amounts of  $\text{C}^{2+}$ , and *ortho*-xylene did not. This might perhaps be related to the effect reported here, but to study this possible connection, it would be highly desirable to obtain not only the fragment charge to mass ratios, but also their fragmentation momenta. This would make it easier to determine if multiple ionization was occurring in the parent prior to dissociation, as observed in our report, or rather is a “final state effect” where the laser ionizes a fragment after dissociation. In our work the parent became multiply charged, leading to high kinetic energy fragments.

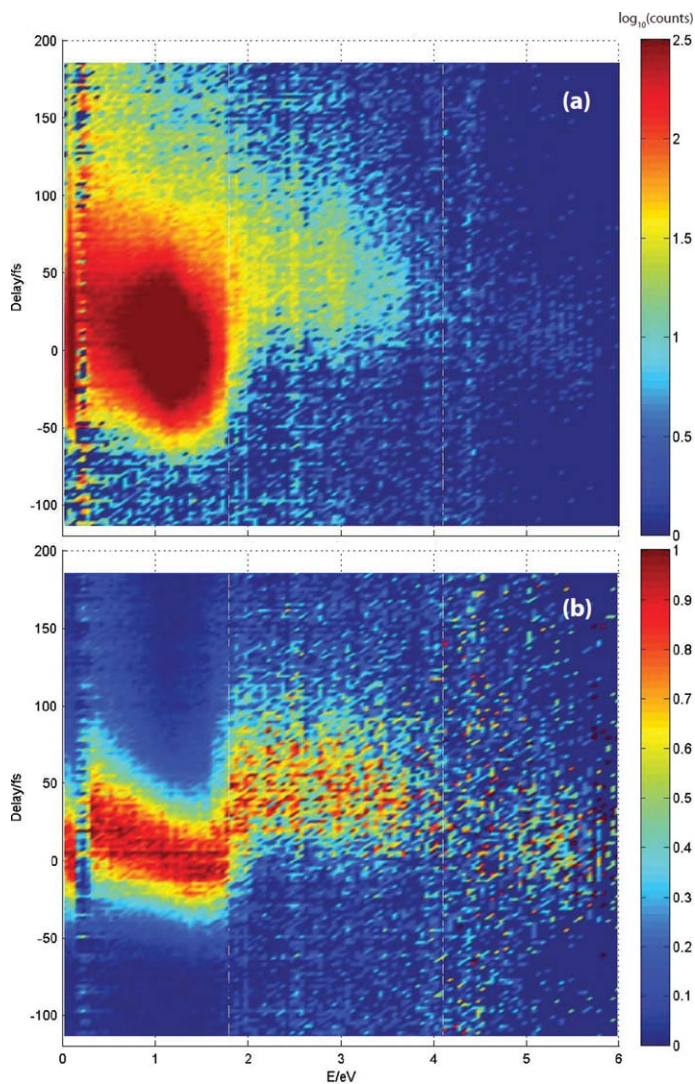
As an aside, White *et al.* [*J. Chem Phys.*, 2012, **136**, 054303] did observe some  $\text{C}^{2+}$  fragmentation in the product isomer 1,3,5-hexatriene, in the spectral unmixing study reported above (see the reply following the comment by Professor Neumark, earlier in this discussion). We may therefore suppose that it may also be present in the experiment of Petrovic *et al.* However, this fragment channel was not studied by Petrovic

**Dr Hockett** gave further comment on the paper by Dr Blancafort: It occurred to me that, since the discussion this week has touched a number of times on the closer integration of experiment and theory, I might show some recent work in order to provide a concrete example to frame this discussion, which was so far very general. This work also serves as an illustration of another, related, topic which came up in several discussions: the quantitative analysis of data from



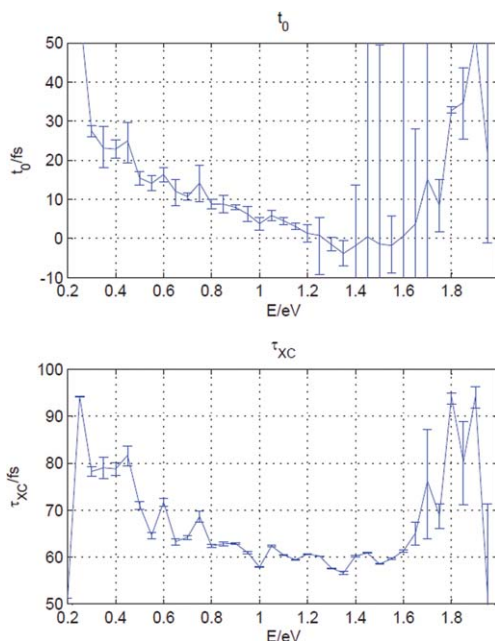
complex dynamical systems, and the utility – or otherwise – of time constants drawn from kinetic models as a metric for such systems.

Fig. 6 shows some recent results from time-resolved photoelectron spectroscopy (TRPES) of butadiene. In this work we were using 200nm to pump, and 266nm to probe; the duration of both pulses was on the order of 40 fs. Detection was *via* a magnetic bottle spectrometer. The spectrum shows a clear stripe of photoelectron signal with “chirp” - a delayed onset of signal as a function of energy. If we look at the same data, normalized for each energy slice, it is clear that the peak shapes are approximately Gaussian for all photoelectron energies, with some broadening towards the lower energy part of the spectrum.



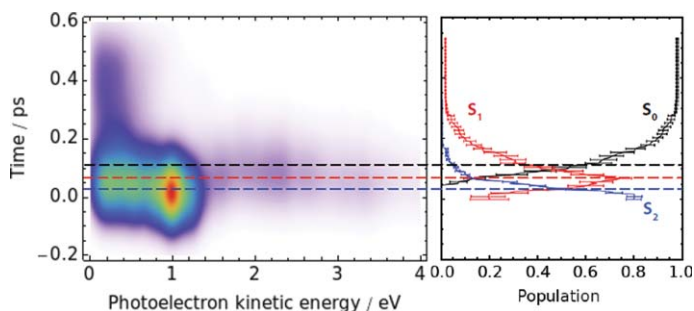
**Fig. 6** (a) time-resolved photoelectron spectrum, colour bar shows  $\log(\text{counts})$ ; (b) same data as (a), but normalized to peak of signal for each energy slice (0.1 eV slices), colour bar shows normalized counts. The 1-photon cut-off is at  $\sim 1.8$  eV, 2-photon cut-off at  $\sim 4.1$  eV.





**Fig. 7** Parameters for Gaussian temporal fits, performed independently for each energy slice. Fits were weighted to the rising edge of the signal, and by experimental uncertainties (statistical). The Gaussian centre is defined by  $t_0$ , and full-width half-max by  $\tau_{XC}$ . Regions with large error bounds indicate low signal or non-Gaussian line-shapes.

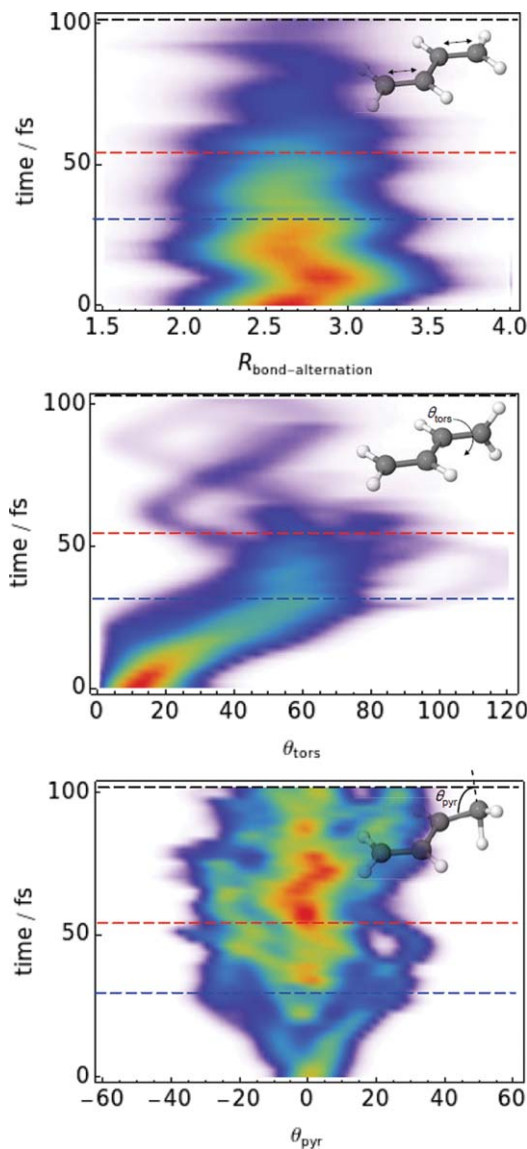
It is clear that “standard” kinetic models, based on two or more analytic temporal functions (usually exponential delays convoluted with a Gaussian cross-correlation feature) with globally fitted time constants and spectral components, aren’t really appropriate for this kind of complex behaviour. In practice a reasonable fit might be found with enough temporal functions, but there is no clear physical significance or import to such a fit (which essentially originates from a statistical picture of the dynamics) – beyond the use of such an analysis as an empirical metric. Therefore, an alternative empirical metric might be considered in order to quantify the observed spectrum, and potentially provide



**Fig. 8** Calculated time-resolved ionization potential (TRIP) from full-dimensional wavepacket calculations and electronic state populations on  $S_2$  (bright state),  $S_1$  and  $S_0$ . Calculations and figure courtesy of M. S. Schuurman (2012, unpublished).

deeper insight into the underlying dynamics in the case where phenomenological inferences may be drawn from such a metric.

Fig. 7 shows the results of Gaussian temporal fits, performed independently for each energy slice. This provides a metric to quantify both the chirp of the spectrum and the broadening observed – hence a way to clock the observed wavepacket dynamics. Here the fitted parameters, as a function of energy, are approximately linear over the observed spectral region, down to around  $E=0.3$  eV where there is significant contribution from background signal. This suggests a



**Fig. 9** Wavepacket dynamics projected onto (a) bond-alternation coordinate, (b) terminal methyl torsion, (c) terminal methyl pyramidalization. Calculations and figure courtesy of M. S. Schuurman (2012, unpublished).

phenomenological picture of the initial wavepacket on the excited state moving rapidly (and with little dispersion) along a steep gradient(s) on the potential energy surface, with this motion mapped primarily to the instantaneous ionization potential. It is important to note that this is a very different picture from that of a kinetic model fit, which would provide two (or more) time constants, often interpreted as indicative of wavepacket dephasing or excited state lifetimes. In this case, such time constants would indicate only the decay of the signal from a given region of the spectrum.

Fig. 8 shows some examples of the results of recent *ab initio* multiple spawning (AIMS) calculations, performed by Michael Schuurman at NRC; these are state-of-the-art, full-dimensionality wavepacket calculations. From these results we can compare directly the experimental TRPES and calculated TRPES or, in this case, the calculated TRIP (time-resolved ionization potential). The TRIP represents a reasonable simplification to obviate calculation of the full ionization matrix elements, and may be a good approximation in many cases. In this case there is, visually, good agreement between theory and experiment. Furthermore, by fitting the calculated TRIP to the models discussed above, a more quantitative comparison can be made, revealing good agreement between the extracted metrics from the calculated and experimental data.

Of course, the benefit of theory is that we can now look behind the curtain at the underlying wavepacket dynamics which give rise to the observable. As was already discussed a little this morning, the understanding, mapping and visualization of multi-dimensional spaces is a hard problem, so we show here just a couple of example projections along key vibrational coordinates. In particular the torsional coordinate shows rapid and irreversible motion, while the carbon backbone shows damped oscillatory behaviour. In this case the steep gradient along the torsional coordinate is primarily responsible for the rapid wavepacket motion observed experimentally, and maps essentially to the IP of the system. Other observables may be sensitive to different aspects/dimensions of the wavepacket motion – for example the photoelectron angular distributions show fast oscillations which appear to map some of the carbon backbone dynamics.<sup>1</sup>

In conclusion, this joint experimental and theoretical study indicates both some of the important issues in moving forward with time-resolved measurements of polyatomic systems – in particular the way we might move towards using more detailed metrics for clocking wavepacket motions – and the benefit of close collaboration between experiment and theory.

1. P. Hockett, E. Ripani, A. Rytwinski and A. Stolow, *Journal of Modern Optics*, 2013, DOI:10.1080/09500340.2013.801525.